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(11) Publication number: 0 261 712 A1

EUROPEAN PATENT APPLICATION

(21) Application number: 87201642.3

(22) Date of filing: 31.08.87

(51) Int. Cl.[4]: G02F 1/133, C09K 19/38, C08F 20/30

(30) Priority: 04.09.86 NL 8602235

(43) Date of publication of application: 30.03.88 Bulletin 88/13

(84) Designated Contracting States: CH DE FR GB LI NL

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(54) Picture display cell, method of forming an orientation layer on a substrate of the picture display cell and monomeric compounds for use in the orientation layer.

(57) The picture display cell comprising two transparent plates having an electrode (4, 5) with thereon an orientation layer (7) and a sealing ring (3) between the ends of the plates, a liquid crystalline (6) material being present in the space between the plates and the ring, the orientation layer being formed from a (methacrylate) monomer or a low molecular compound which is first oriented in a electric or magnetic field after having been transferred in the liquid crystalline phase by raising the temperature.
Then, the polymerization of the oriented monomer takes place by exposure to actinic light (notably UV).

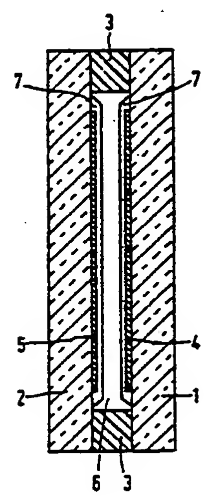

FIG.1

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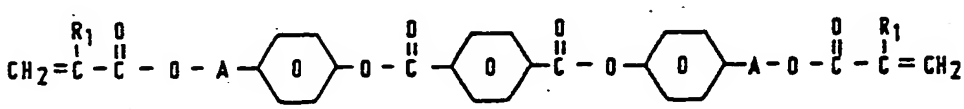

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Picture display cell, method of forming an orientation layer on a substrate of the picture display cell and monomeric compounds for use in the orientation layer.

The invention relates to a picture display cell comprising as a substrate two oppositely relocated plates which are transparent to light and which on the facing sides comprise an electrode of a material which is transparent to light having hereon an orientation layer and a sealing ring between the ends of the plates, a liquid crystalline material being provided in the space between the plates and the ring. The invention further relates to a method of forming an orientation layer on a substrate for the picture display cell comprising an electrode and to the materials from which the orientation layer is manufactured.

Such a picture display cell is known from United States Patent Specification 4,469,409 in which picture display cell an orientation layer is provided on a glass substrate, which orientation layer is formed from a film of a homogeneous mixture having a silanol oligomer modified with an aromatic ring which comprises a silane group and an organic polymer. The picture display cell of the twisted nematic type (TN-type) according to the said United States Patent Specification comprises a substrate having an orientation layer which can better withstand elevated temperatures and has an improved bonding to the substrate than the previously used organic polymers having an imide or quinazoline ring. A method of providing a polymeric layer on a substrate is described in example 1 of the United States Patent Specification in which a solution of the polymer is prepared and this solution is provided on the substrate via a spinning technique.

German Auslegeschrift 2,315,541 discloses a picture display cell in which on the substrate an orientation is provided by vapour deposition at reduced pressure. According to these vapour deposition techniques SiO_x layers are provided and more information on such layers is procured by H.A. van Sprang and R.G. Aartsen in J.Appl.Phys. 56(2), July 15, 1984, pp.251-262, in which general article the method of providing, the measurements and the apparatus used are described. The use of such an SiO_x orientation layer in a picture display cell, however, has for its disadvantage that with these cells only a restricted range of solid angles for the orientation of the nematic liquid crystal material is available.

German Offenlegungschrift 3,020,645 discloses a picture display cell in which a polymeric orientation layer is provided on the substrate, which polymeric orientation layer itself is liquid crystalline. When switching on or of the voltage the liquid crystalline material and the polymeric layer are both oriented at right angles to or parallel to the substrate. The orientation layer is also in the liquid cristalline phase under operating conditions.

Japanese Patent Application Kokai No. 52-146255 discloses a picture display cell having a liquid crystalline material in which the orientation of the liquid crystalline material takes place by incorporating herein magnetic particles, for example, -Fe_2O_3 acicular particles which are oriented by means of a magnet, after which the temperature of the glass plates is raised so that the liquid binder at the raised temperature is made to solidify. In this manner the magnetic particles are fixed and hence also the liquid crystal material. The presence of the acicular -Fe_2O_3-particles in the picture display cell, however, has disadvantages because under the influence of said particles interferences in the light permeability can easily occur.

Applicants have made further research into the orientation layer of the picture display cells and they have found that it is possible to provide a polymeric layer on the substrate, which polymeric layer can be oriented and be fixed after the orientation. As polymers could be used specific materials as described inter alia by R. Simon and H.J. Coles in Mol. Cryst. Liq. Cryst. Vol. 102 (Letters), pp. 43-48. This method yielded good results but a disadvantage was that it took some time, for example, 5 minutes to more than 1 hour, dependent on the polymer used, until the orientation layer had been oriented completely in an electric or magnetic field. It has now proved possible to considerably reduce said time necessary for the orientation, namely to even a few seconds, by composing a picture display cell according to the invention as described in the opening paragraph which is characterized in that the orientation layer is formed from a monomer or lower molecular compound which is first oriented in a field and is then polymerized. According to the invention, the method of forming an orientation layer on a substrate which comprises an electrode for a picture display cell is therefore characterized in that a film of a liquid crystalline monomer is provided, said monomer is oriented at a given angle in a magnetic or an electric field and is then polymerized.

The invention will now be described in greater detail with reference to the ensuing description and the drawing, the Figure of which is cross-sectional view of a picture display cell according to the invention.

Reference numerals 1 and 2 in the Figure denote two oppositely relocated plates which are transparent to light and which are herein after referred to as substrates and which on the facing sides comprise electrodes 4 and 5, for example, manufactured of $In_2O_3SnO_2$. An orientation layer 7 with which preferably nematic liquid crystals 6 can be oriented to provided across said electrodes. The cell is formed by placing the substrates thus formed with electrodes and orientation layer opposite to each other and sealing the aperture by means of a ring and filling the space between the substrates and the ring 3 with the liquid crystalline material 6. In practice, a layer of adhesive of an epoxy compound is often used as the ring 3.

Essentially the invention resides in the fact that a liquid crystalline monomer is provided on a substrate and is oriented in an electric or magnetic field after the liquid crystallime monomer has been provided in a liquid crystalline phase and after the orientation the monomer is polymerized, possibly by exposure to actinic light. Another method is to heat the monomer up to a temperature above the transition nematic-isotropic and then cooling it in the field down to a temperature at which the monomer is again liquid crystalline, after which the polymerization is carried out. Dependent on the angle of the optical axis of the nematic groups the polymer layer induces tilted orientation in the subsequently provided liquid crystal material.

More in particular it has been found that, in order to obtain the orientation layer, there may be started from a liquid film of a crystalline (meth)-acrylate monomer. This monomer can be dissolved and the resulting solution can then be provided on the substrate in the form of a thin film according to a known spinning technique. A suitable group of liquid crystalline acrylate monomers is represented by formula 1 of the formula sheet, in which formula - A - is a flexible spacer, for example,

$\{CH_2\}_x$, $\{CH_2\}_xO$, $\{Si(CH_3)_2\text{-}O\}_x$, with x = 1-15

and $\{CH_2\text{-}CH_2\text{-}O\}_y$, with y = 1 to 8 and - B - is a mesogenic group, for example, a group of formulae 7, 8, 9 or 10, and in which formula 1 R_1 is H or CH_3 and R2 is an alkyl group, an aromatic ring, a cyano group or combination hereof. An useful example of such an acrylate monomer is represented by the formula 4 of the formula sheet.

In a preferred embodiment of the picture display cell according to the invention the liquid crystalline meth(acrylate)monomer corresponds to the formulae 2 and 3 of the formula sheet. The monomers of the formulae 2 and 3 are diacrylates which upon polymenication form a cross-link structure.

The monomers of formulae 2 and 3 are novel products. The invention also relates to these novel products. The monomers of formula 2 can be prepared by a chemical process represented by reaction scheme 12 of the formula sheet. The monomers of formula 3 can be manufactured according to the reaction scheme 13 of the formula sheet. The several reactions are, as usual, performed in the presence of inert organic solvents such as ketonen, ethers or hydrocarbons. The reaction A and B of scheme 12 are performed in the presence of an racine, particularly a mixture (10:1) of triethyamine and 1-dimethylamino-pyridine. The reaction A of scheme 13 is performed in the presence of NaOH and NaI. The reactions C and E of scheme 13 are performed in the presence of amine as denoted above for scheme 12. In schemes 12 and 13, R_1 has the meaning disclosed hereinbefore and .... stands for an alkylene group.

Useful representation of the diacrylate monomers are given by the formulae 5 and 6 of the formula sheet.

For the orientation of the mesogenic groups of the monomer in the electric or the magnetic field, the monomer must be transferred to the liquid crystalline phase, which is possible by raising the temperature. For the acrylate of formula 4, shown on the formula sheet, the transition from crystalline to nematic takes place at 89°C and from the nematic to the isotropic state at 98.5°C upon heating the monomer, while upon cooling the transition from the isotropic state to the nematic state takes place at 98°C, the transition from the nematic to the smectic state at 78°C and from the smectic state to the crystalline state at 49°C. This means that the orientation and the <u>in situ</u> polymerization preferably take place at a temperature of 89-98°C dependent on the desired state of the orientation layer.

For the acrylate monomer shown in the formula sheet by formula 5, the transition in a heating cycle from crystalline to smectic takes place at 17°C and from smectic to nematic at 93°C and from nematic to isotropic at 193°C. Therefore, the orientation for the monomer of formula 4 will take place at a temperature between 77 and 153°C.

The compound of the formula 6 shows a transition from crystalline to nematic at 129°C and from nematic to isotropic at 149°C.

The temperature at which the orientation of the monomer, notably the mesogenic group, has to be carried out may be reduced by using a mixture of monomers in which not only the orientation takes place separately but can also take place at the comparatively low temperature, possibly at ambient

temperature. A further modification is the use of a mixture of polymer in a monomer in which the polymer may be constructed from other monomers than the monomer which is used here as a solvent.

The polymerization of the oriented monomer preferably takes place by exposure to actinic light, notably by exposure to UV-light. The polymerization can be accelerated by adding to the acrylate monomers a small quantity, preferably less than 10 % by weight, of a photo initiator. The polymerization preferably takes place while excluding oxygen. As a result of the polymerization the orientation of the mesogenic groups is fixed so that said anisotropy is maintained within a wide temperature range.

The photo initiators to be used are known and an example hereof is Irgacure 651 (trademark of CIBA-Geigy).

It may be advantageous not to provide the film of the monomer directly on the substrate material but first to provide said substrate material with a bonding layer which may consist of methacryloxypropyl trimethoxysilane or aminopropylsilane. Another embodiment which is to be preferred is to carry out the polymerization in the presence of a photo initiator which, however, is not mixed with the monomer but which photo initiator is bound to the surface so that no changes of the liquid crystalline properties of the monomer are obtained in that it is mixed with the non-liquid crystalline photo initiator and moreover the polymerization then takes place from the surface and the polymer chains are bound to the surface. In this manner it is prevented that the polymer is optionally dissolved in the liquid crystalline material 6 of the display cell.

The photo initiator may be bound to the surface by first providing the substrate according to a known method with a layer of -aminopropylsilane, after which the substrate is immersed in a solution of a photo initiator in THF (tetrahydrofuran), for which purpose a 5 % solution of the photo initiator of formula 9 may be used. At ambient temperature the reaction takes place between aminopropylsilane and the compound of formula 9, so that the substrate is provided with a surface film of a material which comprises both an amino group and a benzophenone group, which amino group has an accelerating effect on the photo initiation of the benzophenone group.

If the actinic radiation is carried out with electron radiation it is not necessary to use an initiator. When the orientation of the mesogenic group in the monomer has to be carried out at a comparatively high temperature, the disadvantage of this is that at the said comparatively high temperature the possibility of polymerization rather occurs so that it is to be preferred to perform the orientation at a comparatively low temperature and then to freeze the oriented monomeric groups by polymerization.

Claims

1. A picture display cell comprising as a substrate two oppositely located plates which are transparent to light and which on the facing sides comprise an electrode of a material which is transparent to light having hereon an orientation layer and a sealing ring between the ends of the plate, a liquid crystalline material being provided in the space between the plates and the ring, characterized in that the orientation layer is formed from a monomer or low molecular compound which is first oriented in a field and is then polymerized.

2. A picture display cell as claimed in Claim 1, characterized in that the orientation layer is built up from a polymer obtained by the polymerization of oriented liquid crystalline (meth)acrylate monomers.

3. A picture display cell as claimed in Claims 1-2, characterized in that the acrylate monomers correspond to formula 1, 2 or 3 of the formula sheet, -A-being a flexible spacer, -B-being a mesogenic group, R representing a hydrogen atom or a methyl group and R_2 representing an alkyl group, an aromatic group, acyane group or combinations thereof.

4. A picture display cell as claimed in Claim 3, characterized in that the acrylate monomers correspond to formula 4, 5 or 6 of the formula sheet.

5. A picture display cell as claimed in Claims 1 to 4, characterized in that the orientation layer is formed from a mixture of two or more monomers which are polymerized.

6. Monomers of formula 2 or 3 of the formula sheet, in which R_1 is H or CH_3, and -A-is a flexible spacer, chosen from the group consisting of $\{CH_2\}_x$, $\{CH_2\}_xO$-, $\{Si(CH_3)_2$-$O\}_x$, wherein x = 1-15 or $\{CH_2$-CH_2-$O\}_y$, wherein y = 1 to 8.

7. A method of forming an orientation layer on a substrate for a picture display cell comprising an electrode, characterized in that a film of a liquid crystalline monomer is provided, said monomer is oriented in a magnetic or electric field at a given angle, and is then polymerized.

7. A method as claimed in Claim 7, characterized in that the polymerization is carried out by exposure to actinic light.

9. A method as claimed in Claims 7-8, characterized in that a photo initiator is added to a monomer in a quantity smaller than 10 % by weight calculated on the monomer.

10. A method as claimed in Claim 7-9, characterized in that monomers are used as stated in Claim 6.

11. A method as claimed in Claim 7-10, characterized in that a bonding layer is formed on the substrate before the monomeric film is provided.

12. A method as claimed in Claim 9, characterized in that the photo initiator is bonded to the surface of the substrate and is not mixed in the monomer.

13. A method as claimed in Claim 12, characterized in that the substrate is provided with a bonding agent, then with a photo initiator, after which a monomeric film is provided and after orientation the polymerization of the monomeric film is carried out under the influence of UV-rays.

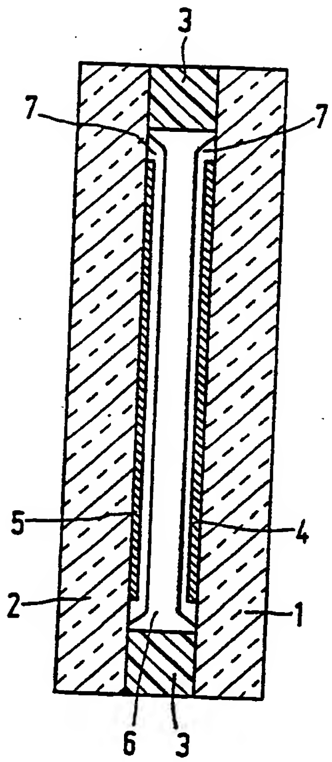
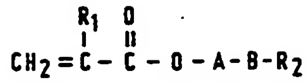
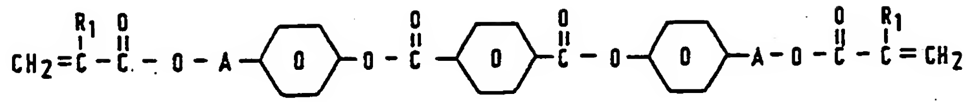
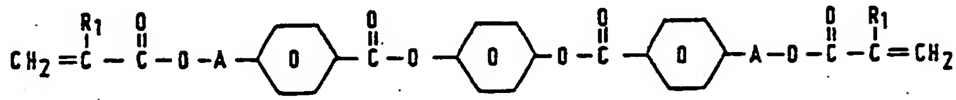
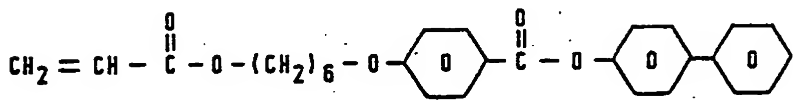


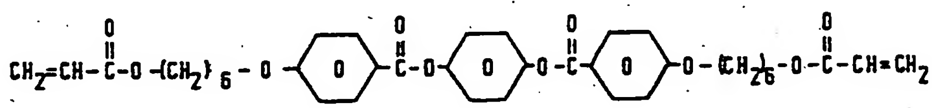
FIG.1

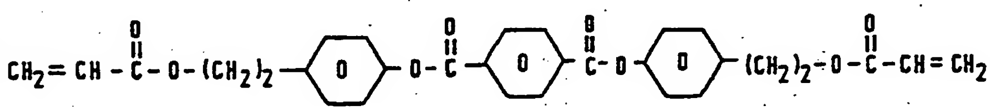
1 

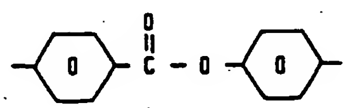
2 

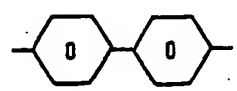
3 

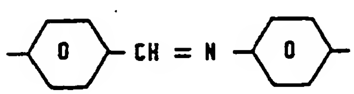
4 

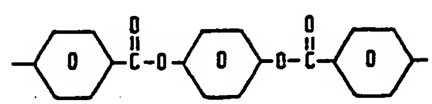
5 

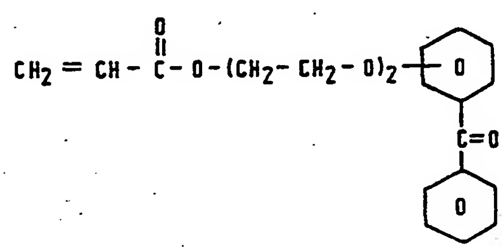
6 

7 

8 

9 

10 

11 

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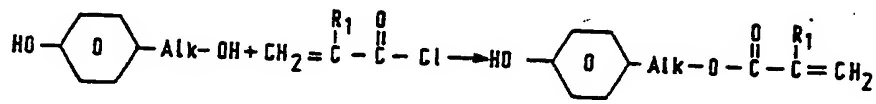

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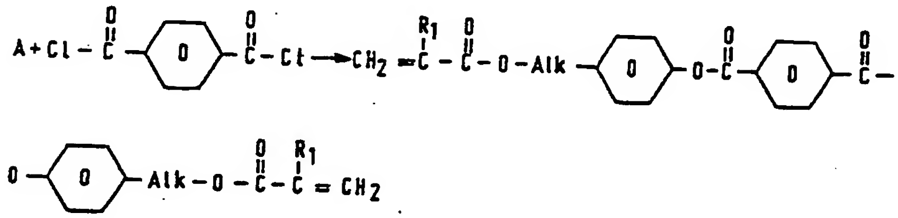

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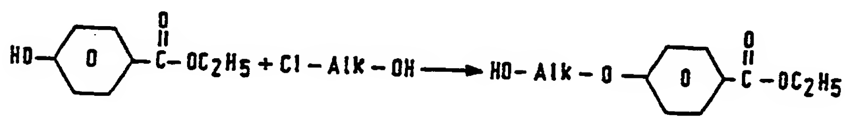

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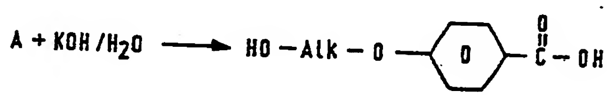

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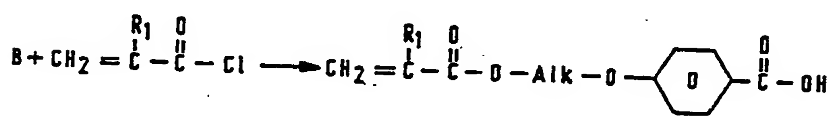

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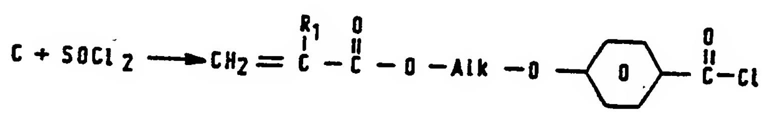

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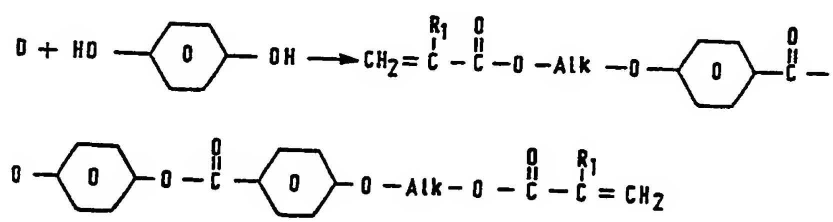

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EUROPEAN SEARCH REPORT

Application Number

EP 87 20 1642

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 137 679 (UNIVERSITY PATENTS INC.) * Page 9, line 5 - page 11, line 7; page 13, lines 17-26 *	1-3,7,8	G 02 F 1/133 C 09 K 19/38 C 08 F 20/30
Y	DE-A-3 027 571 (SIEMENS AG) * Page 8, line 24 - page 9, line 29; page 10, line 24; page 12, line 26 *	1-3,7,8	
A	EP-A-0 184 482 (THOMSON CSF) * Page 11, line 23 - page 13, line 17 *	3	
A	JAPANESE JOURNAL OF APPLIED PHYSICS, vol. 24, no. 11, November 1985, pages 1379-1388, Tokyo, JP; K. MIYANO: "Interfaces as a field for arranging organic molecules" * Chapter 3.3, "Polymerization of monolayers" *	1-3	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

G 02 F 1/00
C 09 K 19/00
C 08 F 20/00
C 08 F 220/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17-12-1987	DIOT P.M.L.

CATEGORY OF CITED DOCUMENTS

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